

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

THIS PAGE BLANK (USPTO)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
12 December 2002 (12.12.2002)

PCT

(10) International Publication Number
WO 02/099014 A2

(51) International Patent Classification⁷: **C10G 65/04**,
45/60, 45/08

(21) International Application Number: **PCT/EP02/06301**

(22) International Filing Date: **7 June 2002 (07.06.2002)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
01401491.4 **7 June 2001 (07.06.2001)** **EP**

(71) Applicant (*for all designated States except US*): **SHELL
INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V. [NL/NL]**; Carel van Bylandtlaan 30, NL-2596 HR
The Hague (NL).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **BENARD, Ger-
ard [FR/FR]**; Route Departementale no. 3, F-76650
Petit Couronne (FR). **DUPREY, Eric [FR/FR]**; Route
Departementale No. 3, F-76650 Petit Couronne (FR).
VAN VEEN, Johannes, Anthonius, Robert [NL/NL];
Badhuisweg 3, NL-1031 CM Amsterdam (NL).

Published:

— *without international search report and to be republished
upon receipt of that report*

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: **PROCESS TO PREPARE A BASE OIL FROM SLACK-WAX**

(57) Abstract: Process to prepare a base oil starting from a slack wax containing feedstock by (a) contacting the feedstock in the presence of hydrogen with a sulphided hydrodesulphurisation catalyst comprising nickel and tungsten on an acid amorphous silica-alumina carrier and (b) performing a pour point reducing step on the effluent of step (a) to obtain the base oil.



WO 02/099014 A2

PROCESS TO PREPARE A BASE OIL FROM SLACK-WAX

The invention is directed to a process to prepare a base oil starting from a slack wax containing feedstock by contacting the feedstock in the presence of hydrogen with a catalyst comprising a Group VIB metal and a non-noble Group VIII metal on an amorphous carrier.

GB-A-1493620 describes a hydroisomerisation process to prepare base oils. The catalysts, which are known to be used in such a reaction generally, comprise a hydrogenation component and an acid component.

GB-A-1493620 discloses a catalyst comprising nickel and tungsten as hydrogenation components, supported on an alumina carrier. The required acidity for the catalyst is provided by the presence of fluorine.

There have been many efforts to obtain a fluorine free hydroisomerisation catalyst. For example WO-A-9941337 describes a hydroisomerisation process wherein a slack-wax containing feed is contacted with a fluorine free catalyst. The disclosed catalyst consists of a platinum or palladium metal on a silica-alumina carrier. According to this publication a hydrotreatment step is preferably performed prior to the hydroisomerisation step in order to reduce the sulphur and nitrogen content to below 2 ppm, in order to avoid deactivation of the noble metal containing hydroisomerisation catalyst.

US-A-5370788 describes a hydroisomerisation catalyst optionally containing fluorine. US-A-5370788 describes a slack wax hydroisomerisation process wherein a non-fluorided nickel-molybdenum on silica-alumina carrier catalyst is used having almost only pores with diameters

between 60-130 Å, a total surface area of 249 m²/g and a total pore volume of 0.5 cc/g, wherein the pore volume of the pores having a pore diameter of above 500 Å is 0.05 cc/g. The catalyst is said to be sulphur tolerant.

5 The highest base oil yield on slack-wax reported in this publication is about 38 wt% obtained when the hydroisomerisation process was performed at about 70 bar and 370 °C.

EP-A-537969 describes a hydroisomerisation catalyst optionally containing fluorine. A slack wax hydroisomerisation process is described wherein a nickel-molybdenum on silica-alumina carrier catalyst is used having almost only pores with diameters below 100 Å, a total surface area of between 100 and 250 m²/g. The catalyst is said to be sulphur tolerant. The high base oil yield on slack-wax are reported in this publication when the hydroisomerisation process was performed at about 70 bar and at temperatures about 400 °C. According to this publication the products require a hydrofinishing

10

15

20 step to improve their UV stability.

EP-A-666894 describes a hydroisomerisation catalyst containing no fluorine. A slack wax hydroisomerisation process is disclosed wherein a nickel-molybdenum on silica-alumina carrier catalyst is used having a certain macroporosity. The macroporosity is defined in that a considerable part of the pores have a diameter greater than 100 nm. The total pore volume is between 0.6 and 1.2 ml/g. The highest base oil yield on slack-wax reported in this publication is about 42 wt% obtained when the hydroisomerisation process was performed at 140 bar and at 391 °C.

25

30

US-A-5292989 describes a wax hydroisomerisation process wherein a catalyst is used comprising cobalt, nickel and molybdenum on a silica-alumina carrier wherein

silica was deposited on the surface of the carrier. Slack wax is, according to the description, a possible feed. The sulphur and nitrogen content in the slack wax feed are preferably reduced to below 2 ppm before hydroisomerisation.

It is an object of the present invention to provide a slack wax hydroisomerisation process, which can be operated at relatively low pressures, i.e. less than 100 bar. A disadvantage of the above-described processes, which also operate at such lower pressures, is that they are performed at relatively high temperatures, i.e. higher than 390 °C. A disadvantage of such higher temperatures is that the level of poly-aromatic (PCA) compounds in the product becomes too high, i.e. higher than 10 mmol/100 grams of product. Additional hydrofinishing will then be required to saturate these PCA compounds to a level lower than 10 mmol/100 grams.

The object of the present invention is to provide a hydroisomerisation process to prepare base oils from slack-wax which can be performed at lower pressures and lower temperatures. A further object is that the product obtained by said process is low in polyaromatic compounds, preferably having a PCA content of less than 10 mmol/100 grams. A related aim is that the products as obtained do not require an additional hydrofinishing step in order to reduce the PCA content. A further aim is to provide a process, which is tolerant for higher levels of sulphur and nitrogen in the feed, such that a prior hydrotreating step is not necessary. Additional advantages of the present invention will become clear from the description.

The above aims are achieved with the following process. Process to prepare a base oil starting from a slack wax containing feedstock by

(a) contacting the feedstock in the presence of hydrogen with a sulphided hydrodesulphurisation catalyst comprising nickel and tungsten on an acid amorphous silica-alumina carrier and

5 (b) performing a pour point reducing step on the effluent of step (a) to obtain the base oil.

Applicants have found that by using a nickel/tungsten containing catalyst having a relatively high hydrodesulphurisation (HDS) activity and an acid
10 amorphous silica-alumina carrier in step (a) a base oil can be prepared in a high yield at low pressures and temperatures, wherein the base oil product has an acceptable content of polyaromatic compounds. With relatively high hydrodesulphurisation activity is here
15 meant a higher activity when compared to state of the art nickel/tungsten containing catalysts. Further advantages will be apparent from the below description.

The slack-wax containing feed may also contain other wax sources, for example Fischer-Tropsch derived wax.
20 Suitably the content of slack-wax in the feed will be more than 50 wt%, preferably more than 80 wt% up to 100 wt%.

The slack-wax is suitably obtained in a solvent dewaxing process, which can be part of a process to
25 prepare base oils. The slack wax thus obtained suitably has a mean boiling point between 400 and 600 °C. The oil content in the wax, as determined by ASTM D721, is suitably between 0 and 50 wt%. The slack-wax feed may contain between 0 and 1 wt% sulphur and between 0 and
30 150 ppm nitrogen. It has been found that the catalyst employed in the process according to the invention is relatively stable when sulphur and/or nitrogen are part of the feed. This is advantageous because a prior desulphurisation step, also referred to as hydrotreating
35 step, can thus be avoided.

If one base oil grade, having for example a specific kinematic viscosity at 100 °C, is made at a time the boiling range of the slack wax feed is preferably rather narrow, more preferably the difference between the temperature at which 10 wt% is recovered and the temperature at which 90 wt% is recovered is preferably between 80 and 160 °C and preferably below 130 °C. If one intends to prepare two or more base oil grades having different viscosity properties at a time a more wider boiling slack wax feed is preferably used. Such a more wider boiling slack wax feed preferably has a difference between the temperature at which 10 wt% is recovered and the temperature at which 90 wt% is recovered of between 170 °C and 300 °C and more preferably between 170 °C and 250 °C. The different base oil grades having a kinematic viscosity at 100 °C of between 2 and 10 cSt and having excellent Noack volatility properties of at most 17 wt% for the lower viscosity grades and even lower for the more heavier viscosity grades may be advantageously be prepared by isolating such grades from preferably the effluent of step (a) by means of a distillation step.

The catalyst employed in step (a) preferably comprises between 2-10 wt% nickel and between 5-30 wt% tungsten.

The sulphided hydrodesulphurisation catalyst used in step (a) has a relatively high hydrodesulphurisation activity. With relatively high activity is here meant a considerably higher activity when compared to state of the art nickel/tungsten containing catalysts based on a silica-alumina carrier. Preferably the hydrodesulphurisation activity of the catalyst is higher than 30% and more preferably below 40%, and most preferably below 35%, wherein the hydrodesulphurisation activity is expressed as the yield in weight percentage

of C₄-hydrocarbon cracking products when thiophene is contacted with the catalyst under standard hydrodesulphurisation conditions. The standard conditions consists of contacting a hydrogen/thiophene mixture with
5 200 mg of a 30-80 mesh sulphided catalyst at 1 bar and 350 °C, wherein the hydrogen rate is 54 ml/min and the thiophene concentration is 6 vol% in the total gas feed.

Catalyst particles are to be used in the test are first crushed and sieved through a 30-80 mesh sieve. The
10 catalyst is then dried for at least 30 minutes at 300 °C before loading 200 mg of dried catalyst into a glass reactor. Then the catalyst is pre-sulphided by contacting the catalyst for about 2 hours with an H₂S/H₂ mixture, wherein the H₂S rate is 8.6 ml/min and the H₂ rate is
15 54 ml/min. The temperature during the pre-sulphiding procedure is raised from room temperature, 20 °C, to 270 °C at 10 °C/min and held for 30 minutes at 270 °C before raising it to 350 °C at a rate of 10 °C/min. During pre-sulphiding nickel and tungsten oxides are
20 converted to the active metal sulphides. After pre-sulphiding the H₂S flow is stopped and H₂ is bubbled at a rate of 54 ml/min through two thermostatted glass vessels containing thiophene. The temperature of the first glass vessel is kept at 25 °C and the temperature of the second
25 glass vessel is kept at 16 °C. As the vapour pressure of thiophene at 16 °C is 55 mmHg, the hydrogen gas that enters the glass reactor is saturated with 6 vol% thiophene. The test is performed at 1 bar and at a
30 temperature of 350 °C. The gaseous products are analysed by an online gas liquid chromatograph with a flame ionisation detector every 30 minutes for four hours.

In order to obtain a reproducible value for the hydrodesulphurisation activity the test values as obtained by the above method are corrected such to

correspond to the hydrodesulphurisation activity of a reference catalyst. The reference catalyst is the commercial C-454 catalyst as obtainable at the date of filing of Criterion Catalyst Company (Houston) and its reference hydrodesulphurisation activity is 22 wt% according to the above test. By testing both the reference catalyst ("test C-454") and the test catalyst ("measured val") one can easily calculate a consistent actual hydrodesulphurisation activity according to the above test with the below equation:

$$\text{Actual activity} = \text{"measured val"} + ((22 - \text{"test C-454"}) / 22) * \text{"measured val"}$$

The hydrodesulphurisation activity of the nickel/tungsten catalyst can be improved by using chelating agents in the impregnation stage of the preparation of the catalyst as for example described by Kishan G., Coulier L., de Beer V.H.J., van Veen J.A.R., Niemantsverdriet J.W., Journal of Catalysis 196, 180-189 (2000). Examples of chelating agents are nitrilotriacetic acid, ethylenediaminetetraacetic acid (EDTA) and 1,2-cyclohexanediamine-N,N,N',N',-tetraacetic acid.

The carrier for the catalyst is amorphous silica-alumina. The term "amorphous" indicates a lack of crystal structure, as defined by X-ray diffraction, in the carrier material, although some short range ordering may be present. Amorphous silica-alumina suitable for use in preparing the catalyst carrier is available commercially. Alternatively, the silica-alumina may be prepared by precipitating an alumina and a silica hydrogel and subsequently drying and calcining the resulting material, as is well known in the art. The carrier is an amorphous silica-alumina carrier. The amorphous silica-alumina preferably contains alumina in an amount in the range of from 5 to 75% by weight, more preferably from 10 to 60% by weight as calculated on the

carrier alone. A very suitable amorphous silica-alumina product for use in preparing the catalyst carrier comprises 45% by weight silica and 55% by weight alumina and is commercially available (ex. Criterion Catalyst Company, USA).

The total surface area of the catalyst as determined by is preferably above 100 m²/g and more preferably between 200 and 300 m²/g. The total pore volume is preferably above 0.4 ml/g. The upper pore volume will be determined by the minimum surface area required. Preferably between 5 and 40 volume percent of the total pore volume is present as pores having a diameter of more than 350 Å. References to the total pore volume are to the pore volume determined using the Standard Test Method for Determining Pore Volume Distribution of Catalysts by Mercury Intrusion Porosimetry, ASTM D 4284-88.

The catalyst is sulphided. Sulphidation of the catalyst may be effected by any of the techniques known in the art, such as ex-situ or in-situ sulphidation. For example, Sulphidation may be effected by contacting the catalyst with a sulphur-containing gas, such as a mixture of hydrogen and hydrogen sulphide, a mixture of hydrogen and carbon disulphide or a mixture of hydrogen and a mercaptan, such as butylmercaptan. Alternatively, sulphidation may be carried out by contacting the catalyst with hydrogen and sulphur-containing hydrocarbon oil, such as sulphur-containing kerosene or gas oil. The sulphur may also be introduced into the hydrocarbon oil by the addition of a suitable sulphur-containing compound, for example dimethyldisulphide or tertiononylpolysulphide.

The feedstock will preferably comprise a minimum amount of sulphur in order to keep the catalyst in a sulphided state. Preferably at least 200 ppm sulphur and

more preferably at least 700 ppm sulphur is present in the feed. It may be therefore be necessary to add additional sulphur, for example as dimethylsulphide, or a sulphur containing co-feed to the feed of step (a) if the
5 slack wax contains a lower level of sulphur. Examples of slack wax feed, which contain lower levels of sulphur, are slack waxes obtained from oil, which has been obtained in a hydrocracking process. Such slack waxes may contain between 10-200 ppm sulphur.

10 The amorphous silica-alumina carrier of the catalyst preferably has a certain minimum acidity or, said in other words, a minimum cracking activity. Examples of suitable carriers having the required activity are described in WO-A-9941337. More preferably the catalyst
15 carrier, after having been calcined, at a temperature of suitably between 400 and 1000 °C, has a certain minimum n-heptane cracking activity as will be described in more detail below.

20 The n-heptane cracking is measured by first preparing a standard catalyst consisting of the calcined carrier and 0.4 wt% platinum. Standard catalysts are tested as 40-80 mesh particles, which are dried at 200 °C before loading in the test reactor. The reaction is carried out in a conventional fixed-bed reactor having a length to
25 diameter ratio of 10 to 0.2. The standard catalysts are reduced prior to testing at 400 °C for 2 hrs at a hydrogen flow rate of 2.24 Nml/min and a pressure of 30 bar. The actual test reaction conditions are:
30 n-heptane/H₂ molar ratio of 0.25, total pressure 30 bar, and a gas hourly space velocity of 1020 Nml/(g.h). The temperature is varied by decreasing the temperature from 400 °C to 200 °C at 0.22 °C/minute. Effluents are analysed by on-line gas chromatography. The temperature at which 40 wt% conversion is achieved is the n-heptane

test value. Lower n-heptane test values correlate with more active catalyst.

Preferred carriers have an n-heptane cracking temperature of less than 360 °C, more preferably less than 350 °C and most preferably less than 345 °C as measured using the above-described test. The minimum n-heptane cracking temperature is preferably more than 310 °C and more preferably greater than 320 °C.

The cracking activity of the silica-alumina carrier can be influenced by, for example, variation of the alumina distribution in the carrier, variation of the percentage of alumina in the carrier, and the type of alumina, as is generally known to one skilled in the art. Reference in this respect is made to the following articles which illustrate the above: Von Bremer H., Jank M., Weber M., Wendlandt K.P., Z. anorg. allg. Chem. 505, 79-88 (1983); Léonard A.J., Ratnasamy P., Declerck F.D., Fripiat J.J., Disc. of the Faraday Soc. 1971, 98-108; and Toba M. et al, J. Mater. Chem., 1994, 4(7), 1131-1135.

The catalyst may also comprise up to 8 wt% of a large pore molecular sieve, preferably an aluminosilicate zeolite. Such zeolites are well known in the art, and include, for example, zeolites such as X, Y, ultrastable Y, dealuminated Y, faujasite, ZSM-12, ZSM-18, L, mordenite, beta, offretite, SSZ-24, SSZ-25, SSZ-26, SSZ-31, SSZ-33, SSZ-35 and SSZ-37, SAPO-5, SAPO-31, SAPO-36, SAPO-40, SAPO-41 and VPI-5. Large pore zeolites are generally identified as those zeolites having 12-ring pore openings. W. M. Meier and D. H. Olson, "ATLAS OF ZEOLITE STRUCTURE TYPES" 3rd Edition, Butterworth-Heinemann, 1992, identify and list examples of suitable zeolites. If a large pore molecular sieve is used then the well-known synthetic zeolite Y as for example described in US-A-3130007 and ultrastable Y zeolite as for example described in US-A-3536605 are suitable

molecular sieves. Other suitable molecular sieves are ZSM-12, zeolite beta and mordenite. Such molecular sieve containing catalysts, containing between 0.1 and 8 wt% of the sieve, are especially used when the reactor
5 containing the catalyst is alternately used as a hydrocracker reactor to prepare middle distillate fuels and as a reactor to prepare base oils.

The catalyst for use in step (a) may be prepared by any of the suitable catalyst preparation techniques known
10 in the art. A preferred method for the preparation of the carrier comprises mulling a mixture of the amorphous silica-alumina and a suitable liquid, extruding the mixture and drying and calcining the resulting extrudates as for example described in EP-A-666894. The extrudates
15 may have any suitable form known in the art, for example cylindrical, hollow cylindrical, multilobed or twisted multilobed. A most suitable shape for the catalyst particles is cylindrical. Typically, the extrudates have a nominal diameter of from 0.5 to 5 mm, preferably from 1
20 to 3 mm. After extrusion, the extrudates are dried. Drying may be effected at an elevated temperature, preferably up to 800 °C, more preferably up to 300 °C. The period for drying is typically up to 5 hours, preferably from 30 minutes to 3 hours. Preferably, the
25 extrudates are calcined after drying. Calcination is effected at an elevated temperature, preferably between 400 and 1000 °C. Calcination of the extrudates is typically effected for a period of up to 5 hours, preferably from 30 minutes to 4 hours. Once the carrier
30 has been prepared, nickel and tungsten may be deposited onto the carrier material. Any of the suitable methods known in the art may be employed, for example ion exchange, competitive ion exchange and impregnation. Preferably nickel and tungsten are added by means of
35 impregnation using a chelating agent as described above.

After impregnation, the resulting catalyst is preferably dried and calcined at a temperature of between 200 and 500 °C.

The hydroisomerisation process is conducted at elevated temperature and pressure. Suitable operating temperatures for the process are in the range of from 290 °C to 370 °C, preferably in the range of from 320 °C to 360 °C. Preferred total pressures are in the range of from 20 to 100 bar and more preferred from 40-90 bar.

Base oil having a viscosity index of between 120-150 can be obtained under these conditions in high yields. The hydrocarbon feed is typically treated at a weight hourly space velocity in the range of from 0.5 to 1.5 kg/l/h, more preferably in the range of from 0.5 to 1.2 kg/l/h.

The feed may be contacted with the catalyst in the presence of pure hydrogen. Alternatively, it may be more convenient to use a hydrogen-containing gas, typically containing greater than 50% vol. hydrogen, more preferably greater than 60% vol hydrogen. A suitable hydrogen-containing gas is gas originating from a catalytic reforming plant. Hydrogen-rich gases from other hydrotreating operations may also be used. The hydrogen-to-oil ratio is typically in the range of from 300 to 5000 l/kg, preferably from 500 to 2500 l/kg, more preferably 500 to 2000 l/kg, the volume of hydrogen being expressed as standard litres at 1 bar and 0 °C.

In step (b) the effluent of step (a) is subjected to a pour point reducing treatment. With a pour point reducing treatment is understood every process wherein the pour point of the base oil is reduced by more than 10 °C, preferably more than 20 °C, more preferably more than 25 °C.

The pour point reducing treatment can be performed by means of a so-called solvent dewaxing process or by means of a catalytic dewaxing process. Solvent dewaxing is well

known to those skilled in the art and involves admixture of one or more solvents and/or wax precipitating agents with the base oil precursor fraction and cooling the mixture to a temperature in the range of from -10 °C to -40 °C, preferably in the range of from -20 °C to -35 °C, to separate the wax from the oil. The oil containing the wax is usually filtered through a filter cloth which can be made of textile fibres, such as cotton; porous metal cloth; or cloth made of synthetic materials. Examples of solvents which may be employed in the solvent dewaxing process are C₃-C₆ ketones (e.g. methyl ethyl ketone, methyl isobutyl ketone and mixtures thereof), C₆-C₁₀ aromatic hydrocarbons (e.g. toluene), mixtures of ketones and aromatics (e.g. methyl ethyl ketone and toluene), autorefrigerative solvents such as liquefied, normally gaseous C₂-C₄ hydrocarbons such as propane, propylene, butane, butylene and mixtures thereof. Mixtures of methyl ethyl ketone and toluene or methyl ethyl ketone and methyl isobutyl ketone are generally preferred. Examples of these and other suitable solvent dewaxing processes are described in Lubricant Base Oil and Wax Processing, Avilino Sequeira, Jr, Marcel Dekker Inc., New York, 1994, Chapter 7.

The wax obtained in the solvent dewaxing step (b) is preferably recycled to step (a).

Alternatively step (b) is performed by means of a catalytic dewaxing process. Such a process is preferred when for example lower pour points are desired than which can be achieved with solvent dewaxing. Pour points of well below -30 °C can be easily achieved. The catalytic dewaxing process can be performed by any process wherein in the presence of a catalyst and hydrogen the pour point of the base oil precursor fraction is reduced as specified above. Suitable dewaxing catalysts are

heterogeneous catalysts comprising a molecular sieve and optionally in combination with a metal having a hydrogenation function, such as the Group VIII metals. Molecular sieves, and more suitably intermediate pore size zeolites, have shown a good catalytic ability to reduce the pour point of the base oil precursor fraction under catalytic dewaxing conditions. Preferably the intermediate pore size zeolites have a pore diameter of between 0.35 and 0.8 nm. Suitable intermediate pore size zeolites are ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35 and ZSM-48. Another preferred group of molecular sieves are the silica-aluminaphosphate (SAPO) materials of which SAPO-11 is most preferred as for example described in US-A-4859311. ZSM-5 may optionally be used in its HZSM-5 form in the absence of any Group VIII metal. The other molecular sieves are preferably used in combination with an added Group VIII metal. Suitable Group VIII metals are nickel, cobalt, platinum and palladium. Examples of possible combinations are Ni/ZSM-5, Pt/ZSM-23, Pd/ZSM-23, Pt/ZSM-48 and Pt/SAPO-11. Further details and examples of suitable molecular sieves and dewaxing conditions are for example described in WO-A-9718278, US-A-5053373, US-A-5252527 and US-A-4574043.

The dewaxing catalyst suitably also comprises a binder. The binder can be a synthetic or naturally occurring (inorganic) substance, for example clay, silica and/or metal oxides. Natural occurring clays are for example of the montmorillonite and kaolin families. The binder is preferably a porous binder material, for example a refractory oxide of which examples are: alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions for example silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-

magnesia and silica-magnesia-zirconia. More preferably a low acidity refractory oxide binder material which is essentially free of alumina is used. Examples of these binder materials are silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of these of which examples are listed above. The most preferred binder is silica.

A preferred class of dewaxing catalysts comprise intermediate zeolite crystallites as described above and a low acidity refractory oxide binder material which is essentially free of alumina as described above, wherein the surface of the aluminosilicate zeolite crystallites has been modified by subjecting the aluminosilicate zeolite crystallites to a surface dealumination treatment. These catalysts may be advantageously used because they allow small amounts of sulphur and nitrogen in the feed. A preferred dealumination treatment is by contacting an extrudate of the binder and the zeolite with an aqueous solution of a fluorosilicate salt as described in for example US-A-5157191 or WO-A-0029511. Examples of suitable dewaxing catalysts as described above are silica bound and dealuminated Pt/ZSM-5, silica bound and dealuminated Pt/ZSM-23, silica bound and dealuminated Pt/ZSM-12, silica bound and dealuminated Pt/ZSM-22, as for example described in WO-A-0029511 and EP-B-832171.

Catalytic dewaxing conditions are known in the art and typically involve operating temperatures in the range of from 200 to 500 °C, suitably from 250 to 400 °C, hydrogen pressures in the range of from 10 to 200 bar. Although lower pressures between 40 to 70 bar are generally preferred for the dewaxing step, the pressure will suitably be in the same range as step (a). Thus when step (a) is performed at a pressure above 70 bar, the dewaxing step will suitably also be performed at a

pressure above 70 bar. The weight hourly space velocities (WHSV) is suitably in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), and preferably from 0.2 to 5 kg/l/hr, more preferably from 0.5 to 3 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2,000 litres of hydrogen per litre of oil.

Before performing a catalytic dewaxing step hydrogen sulphide and ammonia formed in step (a) are preferably removed from the effluent of step (a). This can be performed by for example stripping, preferably using hydrogen as stripping gas.

The effluent of a catalytic dewaxing step (b) is optionally subjected to an additional hydrogenation step (c), also referred to as a hydrofinishing step to saturate any olefins formed in the catalytic dewaxing step. In this hydrogenation step any (poly)aromatic compounds still present in the dewaxed oil can be saturated and/or the oxidative stability of base oil may be improved. This step is suitably carried out at a temperature between 230 and 380 °C, a total pressure of between 10 to 250 bar and preferably above 100 bar and more preferably between 120 and 250 bar. The WHSV (Weight Hourly Space Velocity) ranges from 0.3 to 2 kg of oil per litre of catalyst per hour (kg/l.h).

The hydrogenation catalyst is suitably a supported catalyst comprising a dispersed Group VIII metal. Possible Group VIII metals are cobalt, nickel, palladium and platinum. Cobalt and nickel containing catalysts may also comprise a Group VIB metal, suitably molybdenum and tungsten. Suitable carrier or support materials are low acidity amorphous refractory oxides. Examples of suitable amorphous refractory oxides include inorganic oxides, such as alumina, silica, titania, zirconia, boria, silica-alumina, fluorided alumina, fluorided silica-alumina and mixtures of two or more of these.

Examples of suitable hydrogenation catalysts are nickel-molybdenum containing catalyst such as KF-847 and KF-8010 (AKZO Nobel) M-8-24 and M-8-25 (BASF), and C-424, DN-190, HDS-3 and HDS-4 (Criterion); nickel-tungsten containing catalysts such as NI-4342 and NI-4352 (Engelhard) and C-454 (Criterion); cobalt-molybdenum containing catalysts such as KF-330 (AKZO-Nobel), HDS-22 (Criterion) and HPC-601 (Engelhard). Preferably platinum containing and more preferably platinum and palladium containing catalysts are used. Preferred supports for these palladium and/or platinum containing catalysts are amorphous silica-alumina. Examples of suitable silica-alumina carriers are disclosed in WO-A-9410263. A preferred catalyst comprises an alloy of palladium and platinum preferably supported on an amorphous silica-alumina carrier of which the commercially available catalyst C-624 of Criterion Catalyst Company (Houston, TX) is an example.

The invention will be illustrated with the following non-limiting examples.

Example 1

An LH-21 catalyst as obtained from Criterion Catalyst Company (Houston) was loaded into a reactor and retained as a fixed bed. The LH-21 catalyst had a hydrodesulphurisation activity of 32%. The carrier of this catalyst had a heptane cracking test value of between 320 and 345 °C.

A slack wax, having an oil content of 34.7 wt% (as determined by solvent dewaxing at -27 °C), nitrogen content of 3 mg/kg, a sulphur content of 10 mg/kg and a boiling range:

Initial boiling point	347 °C
30 wt%	468 °C
50 wt%	491 °C
95 wt%	591 °C
Final boiling point	596 °C

was fed to the reactor at a weight hourly space velocity of 1 kg/l/h. The feed was spiked with dimethyldisulphide such that the total content of sulphur in the feed was 0.1 wt%. Hydrogen was fed to the reactor at an inlet pressure of 50 bar and at a flowrate of 1500 Nl/h. The reaction temperature was 350 °C.

The hydrocarbon product was distilled to remove that fraction of the product having a boiling point below 370 °C and further refined by solvent dewaxing at a temperature of -27 °C. The remaining oil was collected. The yield of oil, expressed as wt% of the feed, was 45 wt%. The viscosity index was 138. The kinematic viscosity at 100 °C was 5.1 cSt and at 40 °C was 25 cSt. The content of aromatics, including polyaromatics, was below 6 mmol/100 grams of product.

Example 2

Example 1 was repeated at 90 bar and at 354 °C. The yield of oil, expressed as wt% of the feed, was 40 wt%. The viscosity index was 138 and the content of aromatics, including polyaromatics, was below 2 mmol/100 grams.

Comparative Experiment A

Example 1 was repeated with a commercial fluorided C-454 catalyst as obtained from the Criterion Catalyst Company at 390 °C. The yield of oil, expressed as wt% of the feed, was 47 wt%. A darker base oil product was obtained, wherein the content of mono aromatics was 17.1 mmol/100 g and the amount of diaromatics and polyaromatics was 11.4 mmol/100 g.

C L A I M S

1. Process to prepare a base oil starting from a slack wax containing feedstock by

(a) contacting the feedstock in the presence of hydrogen with a sulphided hydrodesulphurisation catalyst

5 comprising nickel and tungsten on an acid amorphous silica-alumina carrier and

(b) performing a pour point reducing step on the effluent of step (a) to obtain the base oil.

2. Process according to claim 1, wherein the sulphided hydrodesulphurisation catalyst has a

10 hydrodesulphurisation activity of higher than 30%, wherein the hydrodesulphurisation activity is expressed as the yield in weight percentage of C₄-hydrocarbon

15 cracking products when thiophene is contacted with the catalyst under standard hydrodesulphurisation conditions, wherein the standard conditions consist of contacting a hydrogen-thiophene mixture with 200 mg of a 30-80 mesh catalyst at 1 bar and 350 °C, wherein the hydrogen rate is 54 ml/min and the thiophene concentration is 6 vol% in

20 the mixture.
3. Process according to claim 2, wherein the hydrodesulphurisation activity of the catalyst is lower than 40%.

25 4. Process according to any one of claims 1-3, wherein the hydrodesulphurisation catalyst is obtained in a process wherein nickel and tungsten were impregnated on the acid amorphous silica-alumina carrier in the presence of a chelating agent.

30 5. Process according to any one of claims 1-4, wherein the alumina content of the hydrodesulphurisation catalyst

is between 10 and 60 wt% as calculated on the carrier alone.

5 6. Process according to any one of claims 1-5, wherein the silica-alumina carrier has an n-heptane cracking test value of between 310 and 360 °C, wherein the cracking test value is obtained by measuring the temperature at which 40 wt% of n-heptane is converted when contacted, under standard test conditions, with a catalyst consisting of said carrier and 0.4 wt% platinum.

10 7. Process according to claim 6, wherein the silica-alumina carrier has an n-heptane cracking test value of between 320 and 350 °C.

15 8. Process according to any one of claims 1-7, wherein the catalyst comprises between 2-10 wt% nickel and between 5-30 wt% tungsten.

9. Process according to any one of claims 1-8, wherein the surface area of the hydrodesulphurisation catalyst is between 200 and 300 m²/g.

20 10. Process according to any one of claims 1-9, wherein the total pore volume of the hydrodesulphurisation catalyst is above 0.4 ml/g.

25 11. Process according to any one of claims 1-10, wherein between 5 and 40 volume percent of the total pore volume of the hydrodesulphurisation catalyst is present as pores having a pore diameter of more than 350 Å.

12. Process according to any one of claims 1-11, wherein the feedstock in step (a) contains more than 700 ppm sulphur.

30 13. Process according to any one of claims 1-12, wherein the temperature in step (a) is between 320 and 370 °C.

14. Process according to any one of claims 1-13, wherein the pressure in step (a) is between 40 and 90 bar.

15. Process according to any one of claims 1-14, wherein step (b) is performed by means of solvent dewaxing.

16. Process according to claim 15, wherein the wax as obtained by solvent dewaxing is recycled to step (a).

17. Process according to any one of claims 1-14, wherein step (b) is performed by means of catalytic dewaxing.

5 18. Process according to claim 17, wherein the effluent of step (b) is subjected to a hydrogenation step (c).

19. Process according to any one of claims 1-18, wherein the slack wax has a mean boiling point of between 400 and 600 °C and an oil content of between 0 and 50 wt% as
10 determined by ASTM D721.

20. Process according to any one of claims 1-19, wherein the difference between the temperature at which 10 wt% of the slack wax containing feedstock is recovered and the temperature at which 90 wt% of the slack wax containing
15 feedstock is recovered is between 80 and 160 °C.

21. Process according to any one of claims 1-19, wherein the difference between the temperature at which 10 wt% of the slack wax containing feedstock is recovered and the temperature at which 90 wt% of the slack wax containing
20 feedstock is recovered is between 170 and 300 °C.

22. Process according to claim 21, wherein two or more base oils are prepared by isolating two or more intermediate fractions from the effluent of step (a) and performing step (b) on the isolated fractions to obtain
25 the different base oils.

23. Process according to any one of claims 1-22, wherein the base oil as obtained in step (b) has a viscosity index of between 120 and 150.

24. Process according to any one of claims 1-23, wherein
30 the catalyst in step (a) also comprises of up to 8 wt% of a large pore molecular sieve.

25. Process according to claim 24, wherein the large pore molecular sieve is a Y, ultrastable Y, ZSM-12, zeolite beta or mordenite molecular sieve.

26. Process according to any one of claims 24-25, wherein the catalyst of step (a) is alternately used in a process according to any one of the preceding claims and in a process to prepare middle distillate fuels.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
12 December 2002 (12.12.2002)

PCT

(10) International Publication Number
WO 02/099014 A3

(51) International Patent Classification⁷: **C10G 65/04**,
45/60, 45/08, 67/04

(21) International Application Number: PCT/EP02/06301

(22) International Filing Date: 7 June 2002 (07.06.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01401491.4 7 June 2001 (07.06.2001) EP

(71) Applicant (*for all designated States except US*): **SHELL
INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR
The Hague (NL).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **BENARD, Ger-
ard** [FR/FR]; Route Departementale no. 3, F-76650
Petit Couronne (FR). **DUPREY, Eric** [FR/FR]; Route
Departementale No. 3, F-76650 Petit Couronne (FR).
VAN VEEN, Johannes, Anthonius, Robert [NL/NL];
Badhuisweg 3, NL-1031 CM Amsterdam (NL).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Published:

— with international search report

(88) Date of publication of the international search report:
27 November 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS TO PREPARE A BASE OIL FROM SLACK-WAX

(57) Abstract: Process to prepare a base oil starting from a slack wax containing feedstock by (a) contacting the feedstock in the presence of hydrogen with a sulphided hydrodesulphurisation catalyst comprising nickel and tungsten on an acid amorphous silica-alumina carrier and (b) performing a pour point reducing step on the effluent of step (a) to obtain the base oil.

WO 02/099014 A3

INTERNATIONAL SEARCH REPORT

International Application No.

PCV/EP 02/06301

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G65/04 C10G45/60 C10G45/08 C10G67/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 378 351 A (GUICHARD PHILIPPE ET AL) 3 January 1995 (1995-01-03)	1-3,5-9, 11-16, 19,23
Y	column 2, line 1 -column 4, line 25	1,4,16
E	column 6, line 65 -column 7, line 4; claim 1 --- WO 02 46333 A (CHEVRON USA INC) 13 June 2002 (2002-06-13) page 4, line 12 - line 21 page 22; claims 1,2,13; example 1 page 14, line 14 -page 17, line 6 page 6, line 1 - line 27 --- -/--	1-3,6-8, 12-15, 17,18, 20-23



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

8 May 2003

Date of mailing of the international search report

16/05/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Deurinck, P

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/06301

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 5 543 035 A (ZIERER JAMES N) 6 August 1996 (1996-08-06)</p> <p>column 3, line 1 -column 8, line 48; claims 1,6,10,11,16-18; examples 1,2; table 1</p>	<p>1-3, 5-11, 13-15, 17-19, 23-25</p>
X	<p>EP 0 574 191 A (MOBIL OIL CORP) 15 December 1993 (1993-12-15)</p> <p>page 4, line 5 - line 10 page 9, line 1 - line 38; claims 1,7,8; tables 2,4 page 6, line 38 - line 51</p>	<p>1-3, 6-10,13, 17, 19-21,23</p>
X	<p>US 5 951 848 A (DOUGHERTY RICHARD C ET AL) 14 September 1999 (1999-09-14)</p> <p>column 4, line 14 -column 10, line 47; claim 14; tables 1,2</p>	<p>1-3, 6-10,12, 13,15, 17-21</p>
Y	<p>KISHAN G ET AL: "SULFIDATION AND THIOPHENE HYDRODESULFURIZATION ACTIVITY OF NICKEL TUNGSTEN SULFIDE MODEL CATALYSTS, PREPARED WITHOUT AND WITH CHELATING AGENTS" JOURNAL OF CATALYSIS, ACADEMIC PRESS, DULUTH, MN, US, vol. 196, 2000, pages 180-189, XP001151639 ISSN: 0021-9517 cited in the application page 5, line 8 - line 10 page 7, line 187 - line 188</p>	<p>1,4</p>
Y	<p>US 3 830 723 A (LADEUR P ET AL) 20 August 1974 (1974-08-20) column 6, line 11 - line 21</p>	<p>1,16</p>

INTERNATIONAL SEARCH REPORT

tion on patent family members

International Application No

PCT/EP 02/06301

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5378351	A	03-01-1995	AT 148491 T	15-02-1997
			AU 671689 B2	05-09-1996
			AU 5338994 A	24-05-1994
			BR 9307322 A	01-06-1999
			CA 2147986 A1	11-05-1994
			CN 1086248 A , B	04-05-1994
			CZ 9501116 A3	18-10-1995
			DE 69307915 D1	13-03-1997
			DE 69307915 T2	26-06-1997
			DK 666894 T3	17-02-1997
			WO 9410263 A1	11-05-1994
			EP 0666894 A1	16-08-1995
			ES 2098065 T3	16-04-1997
			FI 951991 A	26-04-1995
			HU 71918 A2	28-02-1996
			JP 8503234 T	09-04-1996
			NO 951591 A	27-06-1995
			NZ 257139 A	26-04-1996
			RU 2116332 C1	27-07-1998
			ZA 9307950 A	27-05-1994
WO 0246333	A	13-06-2002	AU 3768602 A	18-06-2002
			AU 9343601 A	06-06-2002
			GB 2374348 A	16-10-2002
			NL 1019472 C2	07-08-2002
			NL 1019472 A1	06-06-2002
			WO 0246333 A2	13-06-2002
US 5543035	A	06-08-1996	AU 692574 B2	11-06-1998
			AU 2909695 A	04-03-1996
			BR 9508454 A	14-07-1998
			CA 2194975 A1	15-02-1996
			CN 1154130 A , B	09-07-1997
			CZ 9700043 A3	11-06-1997
			EP 0775184 A1	28-05-1997
			FI 970395 A	30-01-1997
			HU 77419 A2	28-04-1998
			JP 10503542 T	31-03-1998
			PL 318267 A1	26-05-1997
			RU 2140966 C1	10-11-1999
			SG 32432 A1	13-08-1996
			SK 10697 A3	04-06-1997
			WO 9604354 A1	15-02-1996
EP 0574191	A	15-12-1993	US 5275719 A	04-01-1994
			AU 656267 B2	27-01-1995
			AU 3983393 A	09-12-1993
			CA 2096993 A1	09-12-1993
			DE 69311765 D1	31-07-1997
			DE 69311765 T2	06-11-1997
			EP 0574191 A1	15-12-1993
			ES 2103432 T3	16-09-1997
			JP 6065583 A	08-03-1994
			SG 42945 A1	17-10-1997
US 5951848	A	14-09-1999	AU 717101 B2	16-03-2000
			AU 5004797 A	22-05-1998
			EP 0938532 A1	01-09-1999

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/06301

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5951848	A	JP 2001526706 T WO 9818883 A1	18-12-2001 07-05-1998
US 3830723	A	20-08-1974	
		NL 7204581 A	09-10-1973
		NL 7217257 A	21-06-1974
		AU 470206 B2	04-03-1976
		AU 5411473 A	10-10-1974
		BE 797764 A1	04-10-1973
		CA 1003778 A1	18-01-1977
		DE 2316882 A1	11-10-1973
		DK 140805 B	19-11-1979
		FI 55045 B	31-01-1979
		FR 2179113 A1	16-11-1973
		GB 1429494 A	24-03-1976
		IT 983661 B	11-11-1974
		JP 1128210 C	24-12-1982
		JP 49017403 A	15-02-1974
		JP 57017037 B	08-04-1982
		NO 139741 B	22-01-1979
		SE 396614 B	26-09-1977
		ZA 7302338 A	30-01-1974

THIS PAGE BLANK (USPTO)